PRODUCTION OF FLUORITE AND FLUORITE FOR PHOTOLITHOGRAPHY

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Abstract

PROBLEM TO BE SOLVED: To provide a method for producing a fluorite single crystal, by which a fluorite single crystal having sufficiently small birefringence and capable of using to an optical system in photolithography, especially, having a large aperture (>=200 mm &theta) and good optical characteristic and capable of using to photolithography having <=250 nm wavelength is obtained.

SOLUTION: This method for producing the objective fluorite single crystal comprises heat-treating a fluorite single crystal by a step for housing the fluorite single crystal in a container capable of making the interior airtight, hermetically closing the container, subjecting the interior of the container to vacuum evacuation and raising a temperature in the container to a prescribed temperature (first temperature) lower than a melting point of the fluorite single crystal and a step for retaining the temperature in the container at a prescribed temperature (first temperature) for a prescribed time and a step for lowering the temperature in the container to a room temperature to improve optical characteristics. In this case, maximum temperature in heat treatment is set to a prescribed temperature (first temperature) in the range within 1020 deg.C to 1150 deg.C.

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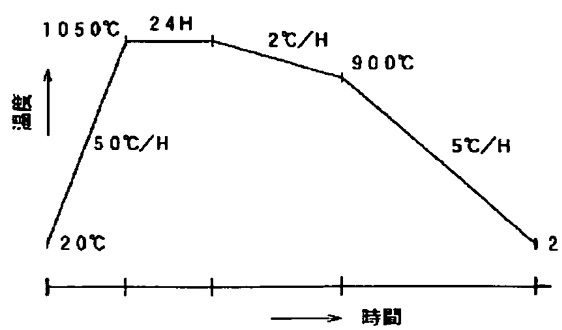
(54)【発明の名称】　蛍石の製造方法及び光リソグラフィー用の蛍石

(57)【要約】
【課題】　複屈折が充分に小さくて、光リソグラフィーにおける光学系に使用可能な蛍石単結晶が得られ、特に波長２５０ｎｍ以下の光リソグラフィーに使用可能な大口径（φ200mm以上）で光学特性が良好な蛍石単結晶が得られる蛍石単結晶の製造方法を提供すること。
【解決手段】　気密化可能な容器内に蛍石単結晶を収納して前記容器を密閉し、前記容器内を真空排気した後に、前記容器の外側に設けられたヒーターにより加熱して、容器内温度を前記蛍石単結晶の融点よりも低い所定温度（第１温度）まで昇温させる工程と、前記容器内温度を前記所定温度（第１温度）に所定の時間、保持する工程と、前記容器内温度を室温まで降温する工程と、により蛍石単結晶を熱処理することで光学特性を向上させた蛍石単結晶を製造する方法において、熱処理の最高温度を1020～1150℃の範囲にある所定温度（第１温度）としたことを特徴とする蛍石単結晶の製造方法。



実施例１に記載の熱処理スケジュール

【特許請求の範囲】

【請求項１】　気密化可能な容器内に蛍石単結晶を収納して前記容器を密閉し、前記容器内を真空排気した後に、
前記容器の外側に設けられたヒーターにより加熱して、容器内温度を前記蛍石単結晶の融点よりも低い所定温度（第１温度）まで昇温させる工程と、前記容器内温度を前記所定温度（第１温度）に所定の時間、保持する工程と、前記容器内温度を室温まで降温する工程と、により蛍石単結晶を熱処理することで光学特性を向上させた蛍石単結晶を製造する方法において、
熱処理の最高温度を1020～1150℃の範囲にある所定温度（第１温度）としたことを特徴とする蛍石単結晶の製造方法。

【請求項２】　気密化可能な第１容器内に、蛍石単結晶及びフッ素化剤を収納した第２容器を設置して前記第１容器を密閉し、前記第１容器内を真空排気した後に、
前記第１容器の外側に設けられたヒーターにより加熱して、第１容器内温度及び／または第２容器内温度を前記蛍石単結晶の融点よりも低い所定温度（第１温度）まで昇温させるとともに、前記第２容器内をフッ素ガス雰囲気とする工程と、前記第１容器内温度及び／または第２容器内温度を前記所定温度（第１温度）に所定の時間、保持する工程と、前記第１容器内温度及び／または第２容器内温度を室温まで降温する工程と、前記第１容器内を大気開放する工程と、により蛍石単結晶を熱処理することで光学特性を向上させた蛍石単結晶を製造する方法において、
熱処理の最高温度を1020～1150℃の範囲にある所定温度（第１温度）としたことを特徴とする蛍石単結晶の製造方法。

【請求項３】　前記最高温度（第１温度）から室温までの冷却速度を２℃/時間以下としたことを特徴とする請求項１または２記載の製造方法。

【請求項４】　前記最高温度（第１温度）から600～800℃の範囲或いは700～900℃の範囲（またはそれらの近辺）にある所定温度（第２温度）までの冷却速度を２℃/時間以下としたことを特徴とする請求項１または２記載の製造方法。

【請求項５】　前記第２温度から室温までの冷却速度を5℃/時間以下としたことを特徴とする請求項４記載の製造方法。

【請求項６】　光リソグラフィー用の光学系に使用可能な大口径（φ200mm以上）の蛍石単結晶が得られることを特徴とする請求項１から５のいずれかに記載の製造方法。

【請求項７】　屈折率差△ｎが2×10^{-6}以下の蛍石単結晶が得られることを特徴とする請求項６記載の製造方法。

【請求項８】　光軸方向における複屈折の値が２nm／cm以下の蛍石単結晶が得られることを特徴とする請求項６または７記載の製造方法。

【請求項９】　光軸方向に垂直な側面方向における複屈折の値が５nm／cm以下の蛍石単結晶が得られることを特徴とする請求項６～８のいずれかに記載の製造方法。

【請求項10】　大口径（φ200mm以上）で光軸方向における複屈折の値が２nm／cm以下である光（波長２５０ｎｍ以下）リソグラフィー用の蛍石単結晶。

【請求項11】　光軸方向に垂直な側面方向における複屈折の値が５nm／cm以下である請求項10記載の蛍石単結晶。

【請求項12】　屈折率差△ｎが2×10^{-6}以下である請求項10または11に記載の蛍石単結晶。

【請求項13】　気密化可能な容器内に蛍石単結晶を収納して前記容器を密閉し、前記容器内を真空排気した後に、
前記容器の外側に設けられたヒーターにより加熱して、容器内温度を前記蛍石単結晶の融点よりも低い所定温度まで昇温させる工程と、前記容器内温度を前記所定温度に所定の時間、保持する工程と、前記容器内温度を室温まで降温する工程と、により蛍石単結晶を熱処理することで光学特性を向上させた蛍石単結晶を製造する方法において、
冷却速度による処理物(蛍石単結晶)の光学特性向上に与える影響が特に大きい高温領域における冷却工程では、冷却を充分にゆっくりと行い、前記影響がそれよりも小さい低温領域（高温領域よりも低温の領域）における冷却工程では、速めに冷却することで、処理物(蛍石単結晶)の光学特性向上効果と生産性（納期及びコスト）とのバランスをとることを特徴とする蛍石単結晶の製造方法。

【請求項14】　気密化可能な容器内に蛍石単結晶を収納して前記容器を密閉し、前記容器内を真空排気した後に、
前記容器の外側に設けられたヒーターにより加熱して、容器内温度を前記蛍石単結晶の融点よりも低い所定温度まで昇温させる工程と、前記容器内温度を前記所定温度に所定の時間、保持する工程と、前記容器内温度を室温まで降温する工程と、により蛍石単結晶を熱処理することで光学特性を向上させた蛍石単結晶を製造する方法において、
熱処理時における蛍石単結晶の酸化を防止するために、前記容器内に不活性ガスを封入し、かつ前記容器内の圧力を１気圧（または略１気圧）に保持して熱処理を行うことを特徴とする蛍石単結晶の製造方法。

【請求項15】　気密化可能な第１容器内に、蛍石単結晶及びフッ素化剤を収納した第２容器を設置して前記第１容器を密閉し、前記第１容器内を真空排気した後に、
前記第１容器の外側に設けられたヒーターにより加熱して、第１容器内温度及び／または第２容器内温度を前記

蛍石単結晶の融点よりも低い所定温度まで昇温させるとともに、前記第２容器内をフッ素ガス雰囲気とする工程と、前記第１容器内温度及び／または第２容器内温度を前記所定温度に所定の時間、保持する工程と、前記第１容器内温度及び／または第２容器内温度を室温まで降温する工程と、前記第１容器内を大気開放する工程と、により蛍石単結晶を熱処理することで光学特性を向上させた蛍石単結晶を製造する方法において、
少なくとも熱処理時における蛍石単結晶の酸化を防止するために、前記フッ素化剤を気化させて前記第２容器内をフッ素ガス雰囲気にし、かつ前記第１容器内の圧力を１気圧（または略１気圧）に保持して熱処理を行うことを特徴とする蛍石単結晶の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、ＫｒＦ、ＡｒＦエキシマレーザーやF_2レーザーを用いた各種機器（例えば、ステッパー、ＣＶＤ装置、核融合装置など）のレンズ、窓材等の光学系に、特に波長２５０ｎｍ以下の光リソグラフィー装置（例えば、ＫｒＦ、ＡｒＦエキシマレーザーやF_2レーザーを用いた光リソグラフィー装置）における光学系に、用いて好適な大口径（φ200mm以上）で光学特性が良好な蛍石単結晶が得られる製造方法と、光（波長２５０ｎｍ以下）リソグラフィー用の蛍石単結晶に関するものである。

【０００２】

【従来の技術】近年において、VLSIはますます高集積化、高機能化され、論理VLSIの分野ではチップ上により大きなシステムが盛り込まれるシステムオンチップ化が進行している。これに伴い、その基板となるシリコン等のウェハ上において、微細加工化及び高集積化が要求されている。そして、シリコン等のウェハ上に集積回路の微細パターンを露光・転写する光リソグラフィーにおいては、ステッパと呼ばれる露光装置が使用されている。

【０００３】VLSIの中でDRAMを例にあげると、近年256M以上の容量が現実のものとなり、加工線幅が0.35μm 以下と微細になっているため、光リソグラフィー技術のかなめであるステッパーの投影レンズには、高い結像性能（解像度、焦点深度）が要求されている。解像度と焦点深度は、露光に用いる光の波長とレンズのＮＡ（開口数）によって決まる。

【０００４】露光波長λが同一の場合には、細かいパターンほど回折光の角度が大きくなるので、レンズのＮＡが大きくなければ回折光を取り込めなくなる。また、露光波長λが短いほど、同一パターンにおける回折光の角度は小さくなるので、レンズのＮＡは小さくてよいことになる。解像度と焦点深度は、次式により表される。

【０００５】解像度＝ｋ1 ・λ／ＮＡ

焦点深度＝ｋ2 ・λ／（ＮＡ）^{2}

（ここで、ｋ1 、ｋ2 は比例定数）

上式より、解像度を向上させるためには、レンズのＮＡを大きくする（レンズを大口径化する）か、或いは露光波長λを短くすればよく、またλを短くする方が焦点深度の点で有利であることが判る。

【０００６】まず、光の短波長化について述べると、露光波長λがしだいに短波長となり、ＫｒＦエキシマレーザー光（波長248nm ）を光源とするステッパーも市場に登場するようになってきた。250 nm以下の短波長領域においては、光リソグラフィー用として使える光学材料は非常に少なく、蛍石及び石英ガラスの２種類の材料が用いられている。

【０００７】次に、レンズの大口径化について述べると、単に大口径であればよいというものではなく、屈折率の均質性等の光学特性に優れた石英ガラスや蛍石単結晶が要求される。ここで、従来の蛍石単結晶の製造方法（一例）を示す。蛍石単結晶は、ブリッジマン法（ストックバーガー法、ルツボ降下法）により製造されている。

【０００８】紫外域または真空紫外域において使用される蛍石単結晶の場合、原料として天然の蛍石を使用することはなく、化学合成により作製された高純度原料を使用することが一般的である。原料は粉末のまま使用することが可能であるが、この場合、熔融したときの体積減少が激しいため、半熔融品やその粉砕品を用いるのが普通である。

【０００９】まず、育成装置の中に前記原料を充填したルツボを置き、育成装置内を10^{-3}～10^{-4}Ｐａの真空雰囲気に保持する。次に、育成装置内の温度を蛍石の融点以上まで上昇させてルツボ内の原料を熔融する。この際、育成装置内温度の時間的変動を抑えるために、定電力出力による制御または高精度なＰＩＤ制御を行う。

【００１０】結晶育成段階では、0.1 ～５ｍｍ／ｈ程度の速度でルツボを引き下げることにより、ルツボの下部から徐々に結晶化させる。融液最上部まで結晶化したところで結晶育成は終了し、育成した結晶（インゴット）が割れないように、急冷を避けて簡単な徐冷を行う。育成装置内の温度が室温程度まで下がったところで、装置を大気開放してインゴットを取り出す。

【００１１】サイズの小さい光学部品や均質性の要求されない窓材などに用いられる蛍石の場合には、インゴットを切断した後、丸めなどの工程を経て最終製品まで加工される。これに対して、ステッパーの投影レンズなどに用いられ、高均質が要求される蛍石単結晶の場合には、インゴットのまま簡単なアニールが行われる。そして、目的の製品別に適当な大きさに切断加工された後、さらにアニールが行われる。

【００１２】ところで、特開平8-5801号公報には、光リソグラフィー用の蛍石が記載され、350nm以下の特定波長帯域で使用される場合に、3座標方向のいずれの方向においても複屈折による光路差が10nm/cm以下である蛍

石が開示されている。光路差が光学系の結像性能に与える影響は、波長の何倍であるかという数値で表され（例えばλ/10など）、その係数が小さいほど影響は少ない。例えば、光路差10nmの場合に、波長λ=248nmでは光路差は10/248=0.040λであり、λ=193nmでは光路差は10/193=0.052λとなる。

【0013】即ち、同じ光路差の10nmであっても効果としては、λ=193nmの方が影響が大きく、結像性能は悪化する。そのため、次世代のArFエキシマレーザー(波長193nm）を用いたステッパーの投影レンズにおいては、光路差10nm/cmではまだ不十分であり、複屈折による光路差がさらに小さい蛍石が必要とされている。

【0014】なお、以下においては、複屈折による単位長さあたりの光路差のことを単に複屈折と呼ぶ。また、この複屈折のことを一般的には歪と呼ぶことも多い。これは材料自体に複屈折がない場合でも、歪によって複屈折を生ずることが多いためである。

【0015】

【発明が解決しようとする課題】前述したように、蛍石はブリッジマン法により製造されている。そして、通常のブリッジマン法により蛍石を成長させた後は、蛍石が割れない程度に（或いは切断が可能な程度に）徐冷し、インゴットとして取り出す。インゴットから目的とするサイズに直接切り出すこともあるが、体積が増大すればするほど複屈折や屈折率不均質が大きくなるため、複数のブロックに切断後、さらに熱処理工程にかけることで品質を向上させている。

【0016】この熱処理工程の期間は、生産性を鑑みて従来では1週間から2週間程度が一般的であり、そのため、熱処理工程全体に対する時間占有率が大きい冷却過程（工程）での冷却速度を10℃/H～5℃/Hとしていた。しかしながら、このような蛍石単結晶のアニール（熱処理）により得られた蛍石単結晶は、屈折率の均質性が悪く、また複屈折が大きすぎるという問題点があった。

【0017】そのため、光リソグラフィーにおける光学系に使用できる蛍石単結晶が得られ難く、特に波長250nm以下の光リソグラフィーに使用できる大口径（φ200mm以上）の蛍石単結晶が得られないという問題点があった。本発明は、かかる問題点に鑑みてなされたものであり、蛍石単結晶を熱処理することにより、屈折率の均質性がよく、複屈折が充分に小さくて、光リソグラフィーにおける光学系に使用可能な蛍石単結晶が得られ、特に波長250nm以下の光リソグラフィーに使用可能な大口径（φ200mm以上）で光学特性が良好な蛍石単結晶が得られる蛍石単結晶の製造方法を提供することを目的とする。

【0018】或いは、本発明は前記大口径（φ200mm以上）で光学特性が良好な蛍石単結晶が得られるという効果を奏するだけでなく、かかる効果と生産性とのバランスがとれた蛍石単結晶の製造方法を提供することを目的とする。或いは、本発明は光（波長250nm以下）リソグラフィー用の蛍石単結晶を提供することを目的とする。

【0019】

【課題を解決するための手段】そのため、本発明は第一に「気密化可能な容器内に蛍石単結晶を収納して前記容器を密閉し、前記容器内を真空排気した後に、前記容器の外側に設けられたヒーターにより加熱して、容器内温度を前記蛍石単結晶の融点よりも低い所定温度（第1温度）まで昇温させる工程と、前記容器内温度を前記所定温度（第1温度）に所定の時間、保持する工程と、前記容器内温度を室温まで降温する工程と、により蛍石単結晶を熱処理することで光学特性を向上させた蛍石単結晶を製造する方法において、熱処理の最高温度を1020～1150℃の範囲にある所定温度（第1温度）としたことを特徴とする蛍石単結晶の製造方法（請求項1）」を提供する。

【0020】また、本発明は第二に「気密化可能な第1容器内に、蛍石単結晶及びフッ素化剤を収納した第2容器を設置して前記第1容器を密閉し、前記第1容器内を真空排気した後に、前記第1容器の外側に設けられたヒーターにより加熱して、第1容器内温度及び／または第2容器内温度を前記蛍石単結晶の融点よりも低い所定温度（第1温度）まで昇温させるとともに、前記第2容器内をフッ素ガス雰囲気とする工程と、前記第1容器内温度及び／または第2容器内温度を前記所定温度（第1温度）に所定の時間、保持する工程と、前記第1容器内温度及び／または第2容器内温度を室温まで降温する工程と、前記第1容器内を大気開放する工程と、により蛍石単結晶を熱処理することで光学特性を向上させた蛍石単結晶を製造する方法において、熱処理の最高温度を1020～1150℃の範囲にある所定温度（第1温度）としたことを特徴とする蛍石単結晶の製造方法（請求項2）」を提供する。

【0021】また、本発明は第三に「前記最高温度（第1温度）から室温までの冷却速度を2℃/時間以下としたことを特徴とする請求項1または2記載の製造方法（請求項3）」を提供する。また、本発明は第四に「前記最高温度（第1温度）から600～800℃の範囲或いは700～900℃の範囲（またはそれらの近辺）にある所定温度（第2温度）までの冷却速度を2℃/時間以下としたことを特徴とする請求項1または2記載の製造方法（請求項4）」を提供する。

【0022】また、本発明は第五に「前記第2温度から室温までの冷却速度を5℃/時間以下としたことを特徴とする請求項4記載の製造方法（請求項5）」を提供する。また、本発明は第六に「光リソグラフィー用の光学系に使用可能な大口径（φ200mm以上）の蛍石単結晶が得られることを特徴とする請求項1から5のいずれかに記載の製造方法（請求項6）」を提供する。

【0023】また、本発明は第七に「屈折率差△nが2×10^{-6}以下の蛍石単結晶が得られることを特徴とする請求項6記載の製造方法（請求項7）」を提供する。また、本発明は第八に「光軸方向における複屈折の値が2nm／cm以下の蛍石単結晶が得られることを特徴とする請求項6または7記載の製造方法（請求項8）」を提供する。

【0024】また、本発明は第九に「光軸方向に垂直な側面方向における複屈折の値が5nm／cm以下の蛍石単結晶が得られることを特徴とする請求項6～8のいずれかに記載の製造方法（請求項9）」を提供する。また、本発明は第十に「大口径（φ200mm以上）で光軸方向における複屈折の値が2nm／cm以下である光（波長250nm以下）リソグラフィー用の蛍石単結晶（請求項10）」を提供する。

【0025】また、本発明は第十一に「光軸方向に垂直な側面方向における複屈折の値が5nm／cm以下である請求項10記載の蛍石単結晶（請求項11）」を提供する。また、本発明は第十二に「屈折率差△nが2×10^{-6}以下である請求項10または11に記載の蛍石単結晶（請求項12）」を提供する。また、本発明は第十三に「気密化可能な容器内に蛍石単結晶を収納して前記容器を密閉し、前記容器内を真空排気した後に、前記容器の外側に設けられたヒーターにより加熱して、容器内温度を前記蛍石単結晶の融点よりも低い所定温度まで昇温させる工程と、前記容器内温度を前記所定温度に所定の時間、保持する工程と、前記容器内温度を室温まで降温する工程と、により蛍石単結晶を熱処理することで光学特性を向上させた蛍石単結晶を製造する方法において、冷却速度による処理物(蛍石単結晶)の光学特性向上に与える影響が特に大きい高温領域における冷却工程では、冷却を充分にゆっくりと行い、前記影響がそれよりも小さい低温領域（高温領域よりも低温の領域）における冷却工程では、速めに冷却することで、処理物(蛍石単結晶)の光学特性向上効果と生産性（納期及びコスト）とのバランスをとることを特徴とする蛍石単結晶の製造方法（請求項13）」を提供する。

【0026】また、本発明は第十四に「気密化可能な容器内に蛍石単結晶を収納して前記容器を密閉し、前記容器内を真空排気した後に、前記容器の外側に設けられたヒーターにより加熱して、容器内温度を前記蛍石単結晶の融点よりも低い所定温度まで昇温させる工程と、前記容器内温度を前記所定温度に所定の時間、保持する工程と、前記容器内温度を室温まで降温する工程と、により蛍石単結晶を熱処理することで光学特性を向上させた蛍石単結晶を製造する方法において、熱処理時における蛍石単結晶の酸化を防止するために、前記容器内に不活性ガスを封入し、かつ前記容器内の圧力を1気圧（または略1気圧）に保持して熱処理を行うことを特徴とする蛍石単結晶の製造方法（請求項14）」を提供する。

【0027】また、本発明は第十五に「気密化可能な第1容器内に、蛍石単結晶及びフッ素化剤を収納した第2容器を設置して前記第1容器を密閉し、前記第1容器内を真空排気した後に、前記第1容器の外側に設けられたヒーターにより加熱して、第1容器内温度及び／または第2容器内温度を前記蛍石単結晶の融点よりも低い所定温度まで昇温させるとともに、前記第2容器内をフッ素ガス雰囲気とする工程と、前記第1容器内温度及び／または第2容器内温度を前記所定温度に所定の時間、保持する工程と、前記第1容器内温度及び／または第2容器内温度を室温まで降温する工程と、前記第1容器内を大気開放する工程と、により蛍石単結晶を熱処理することで光学特性を向上させた蛍石単結晶を製造する方法において、少なくとも熱処理時における蛍石単結晶の酸化を防止するために、前記フッ素化剤を気化させて前記第2容器内をフッ素ガス雰囲気にし、かつ前記第1容器内の圧力を1気圧（または略1気圧）に保持して熱処理を行うことを特徴とする蛍石単結晶の製造方法（請求項15）」を提供する。

【0028】

【発明の実施の形態】蛍石単結晶の光学特性を向上させる（例えば複屈折を小さくする）ために行う熱処理（アニール）は、どのような装置や雰囲気で行われるかだけでなく、どのようなスケジュールで行われるかが重要なポイントとなる。例えば、熱処理の最高温度は何℃であり、室温から最高温度まで何時間で昇温させるか、また最高温度で何時間保持したのち、何時間で室温まで冷却させるか、といったスケジュールが重要となる。

【0029】そこで、本発明者らが鋭意研究したところ、最高温度としては、1020～1150℃が最適であることを見いだした。即ち、1150℃以上では蛍石内部に散乱原因となる欠陥が生成し易くなり、1020℃以下では光学特性の向上に与えるアニール効果が少ないことが判った。そこで、本発明（請求項1～9）にかかる製造方法では、熱処理の最高温度を1020～1150℃の範囲にある所定温度（第1温度）とした。

【0030】そして、本発明（請求項1～9）によれば、屈折率の均質性がよく、複屈折が充分に小さくて、光リソグラフィーにおける光学系に使用可能な蛍石単結晶が得られ、特に波長250nm以下の光リソグラフィーに使用可能な大口径（φ200mm以上）で光学特性が良好な蛍石単結晶が得られる。なお、前記最高温度の保持時間は、例えば24時間程度であればよいが、処理物(蛍石単結晶)の口径や体積が大きくなれば長くすることが好ましい。

【0031】また、室温から最高温度に至る昇温速度は、熱衝撃による処理物(蛍石単結晶)への悪影響が発生しない範囲にて設定するとよい。次に、前記最高温度に所定時間保持した後の冷却工程であるが、処理物(蛍石単結晶)の光学特性向上にはこの工程が特に重要であ

る。即ち、冷却速度を遅くすればするほど光学特性の向上効果は大きくなり、逆に冷却速度が速すぎると、充分な効果が得られない。

【００３２】そこで、本発明（請求項３）にかかる製造方法では、前記最高温度（第１温度）から室温までの冷却速度を２℃/時間以下とした。また、本発明者らは、最高温度から600～800℃の範囲（またはその近辺）或いは700～900℃の範囲（またはその近辺）にある所定温度（第２温度）に至る高温領域の冷却工程における冷却速度が処理物(蛍石単結晶)の光学特性向上に与える影響が特に大きいことを見いだした。

【００３３】そこで、本発明（請求項４）にかかる製造方法では、前記最高温度（第１温度）から600～800℃の範囲或いは700～900℃の範囲（またはそれらの近辺）にある所定温度（第２温度）までの冷却速度を２℃/時間以下とした。本発明（請求項３、４）によれば、波長２５０ｎｍ以下の光リソグラフィーに使用可能な大口径（φ200mm以上）で光学特性が極めて良好な蛍石単結晶が得られる。

【００３４】ところで、冷却時間の長さは生産性（納期及びコスト）に大きく影響するので、その点からはできる限り冷却時間が短い（冷却速度が速い）方がよい。そこで、本発明者らは、冷却速度による処理物(蛍石単結晶)の光学特性向上に与える影響が特に大きい高温領域における冷却工程では、前述したように冷却を充分にゆっくりと行うが、前記影響がそれよりも小さい低温領域（高温領域よりも低温の領域）における冷却工程では、速めに冷却することで、処理物(蛍石単結晶)の光学特性向上効果と生産性（納期及びコスト）とのバランスをとることとした（請求項13）。

【００３５】具体的には、本発明（請求項５）にかかる製造方法では、前記最高温度（第１温度）から600～800℃の範囲或いは700～900℃の範囲（またはそれらの近辺）にある所定温度（第２温度）までの高温領域における冷却速度を２℃/時間以下とし、さらに前記第２温度から室温までの低温領域における冷却速度を5℃/時間以下とした。

【００３６】そのため、本発明（請求項５）によれば、大口径（φ200mm以上）で光学特性が良好な蛍石単結晶が得られるという前記効果を奏するだけでなく、かかる効果と生産性とのバランスをとることができる。このように、大口径（φ200mm以上）の蛍石にかかる熱処理においては、冷却速度による処理物(蛍石単結晶)の光学特性向上に与える影響が特に大きい高温領域の冷却工程では、非常にゆっくりと冷却する（冷却速度：２℃/時間以下）ことが重要である。

【００３７】例えば、後述する比較例のように、最高温度から900℃まで（高温領域）を３℃/時間という速すぎる速度で冷却したのでは、光学特性が良好な蛍石が得られない。また、その後の低温領域における冷却工程でも、あまり急激に冷却することは避けた方がよい。

【００３８】なお、処理物(蛍石単結晶)の大型化に伴い、高温領域及び／または低温領域における冷却工程（特に高温領域における冷却工程）を単段階（冷却速度が一種類）から複数段階（冷却速度が二種類以上）とすることが好ましい。即ち、処理物(蛍石単結晶)が大型化するにつれて、生産性（納期及びコスト）を充分に満たす範囲内で、高温領域及び／または低温領域における冷却工程（特に高温領域における冷却工程）を細分化する（単段階における冷却速度よりも遅い速度の冷却工程を一または二以上付加する）ことが好ましい。

【００３９】なお、この場合には、細分化の数の増大に伴って高温領域全体及び／または低温領域全体の温度範囲を拡張してもよい。また、処理物(蛍石単結晶)の大型化に伴い、生産性（納期及びコスト）を充分に満たす範囲内で、第２温度が含まれる温度範囲をより高い範囲に設定（高温側へシフト）したり、温度範囲を縮小するすることが好ましい。

【００４０】例えば、600～800℃の範囲或いは700～900℃の範囲（またはそれらの近辺）と設定した第２温度が含まれる温度範囲を処理物(蛍石単結晶)の大型化に伴って、生産性（納期及びコスト）を充分に満たす範囲内で、650～850℃、750～950℃、700～800℃、800～900℃、800～850℃、850～900℃、900～950℃等のように高い範囲や狭い範囲に変更することが好ましい。

【００４１】或いは、処理物(蛍石単結晶)の大型化に伴い、生産性（納期及びコスト）を充分に満たす範囲内で、冷却工程の細分化、第２温度が含まれる温度範囲の拡張または縮小、各温度領域の高温側へのシフトを適宜組み合わせることが好ましい。かかる構成にするごとにより、処理物(蛍石単結晶)が更に大型化しても、波長２５０ｎｍ以下の光リソグラフィーに使用可能な大口径で光学特性が良好な蛍石単結晶を得られるばかりか、生産性（納期及びコスト）をも充分に満たすことができる。

【００４２】本発明（請求項13）にかかる蛍石単結晶の製造方法は、波長２５０ｎｍ以下の光リソグラフィー用の光学系に使用可能な大口径（φ200mm以上）の蛍石単結晶を得る場合に有効である。本発明（請求項13）にかかる蛍石単結晶の製造方法は、波長２５０ｎｍ以下の光リソグラフィー用の光学系に使用可能な屈折率差△ｎが$２×１０^{-6}$以下で大口径（φ200mm以上）の蛍石単結晶を得る場合に有効である。

【００４３】本発明（請求項13）にかかる蛍石単結晶の製造方法は、波長２５０ｎｍ以下の光リソグラフィー用の光学系に使用可能な光軸方向における複屈折の値が２nm／cm以下で大口径（φ200mm以上）の蛍石単結晶を得る場合に有効である。また、本発明（請求項13）にかかる蛍石単結晶の製造方法は、波長２５０ｎｍ以下の光リソグラフィー用の光学系に使用可能な光軸方向に垂直な側面方向における複屈折の値が５nm／cm以下で大口径

（φ200mm以上）の蛍石単結晶を得る場合に有効である。

【００４４】本発明（請求項１～５）にかかる蛍石単結晶の製造方法は、波長２５０ｎｍ以下の光リソグラフィー用の光学系に使用可能な大口径（φ200mm以上）の蛍石単結晶を得る場合に有効である（請求項６）。また、本発明（請求項１～５）にかかる蛍石単結晶の製造方法は、波長２５０ｎｍ以下の光リソグラフィー用の光学系に使用可能な屈折率差△ｎが2×10^{-6}以下で大口径（φ200mm以上）の蛍石単結晶を得る場合に有効である（請求項７）。

【００４５】また、本発明（請求項１～５）にかかる蛍石単結晶の製造方法は、波長２５０ｎｍ以下の光リソグラフィー用の光学系に使用可能な光軸方向における複屈折の値が2nm／cm以下で大口径（φ200mm以上）の蛍石単結晶を得る場合に有効である（請求項８）。また、本発明（請求項１～５）にかかる蛍石単結晶の製造方法は、波長２５０ｎｍ以下の光リソグラフィー用の光学系に使用可能な光軸方向に垂直な側面方向における複屈折の値が５nm／cm以下で大口径（φ200mm以上）の蛍石単結晶を得る場合に有効である（請求項９）。

【００４６】このように、本発明により、φ200mm以上の大きな蛍石においてはこれまで不可能であった複屈折の小さい蛍石を得ることが可能となり、光（波長２５０ｎｍ以下）リソグラフィー用の蛍石（例えば投影レンズに使用する）として実用に耐えるものが供給できるようになった。また、屈折率の均質性に関しても、充分な均質度に達するものであった。

【００４７】即ち、請求項10～12に記載された複屈折の値が小さくかつ大口径（φ200mm以上）の光（波長２５０ｎｍ以下）リソグラフィー用の蛍石単結晶は、これまでは得られなかったが、本発明（請求項１～９、13）により製造可能となった。なお、直径200mm、厚さ50mmの素材（蛍石）に関して、複屈折の測定を平面に垂直な方向(これを光軸方向と呼ぶ)と、それに垂直な方向（これを側面方向と呼ぶ)について行ったところ、側面方向においては360度の回転があるが、測定をしてみるとほぼ同じ値になることがわかった。

【００４８】また、光軸方向と側面方向では、単位長さあたりの光路差として、側面方向の方が2倍以上大きいこともわかった。熱処理を行って光学特性が良好な蛍石を得るための本発明にかかる製造装置は、処理物（蛍石）を囲む容器を有し、その外側に加熱手段を有するものがよい。また、熱処理中は、処理物（蛍石）に温度むらがないことが望ましい。

【００４９】熱処理の雰囲気については、空気中では700℃以上で蛍石の酸化反応が進むため、不活性ガスの雰囲気、真空雰囲気、またはフッ素ガス雰囲気で行うが、高温状態下における大気圧（容器外）と容器内圧力との圧力差による熱処理容器（気密化可能な容器または第１容器）の変形や破壊を防止して、その結果、光（波長２５０ｎｍ以下）リソグラフィー用の蛍石単結晶が安定して得られるように、前記容器内または第１容器内の圧力を大気圧に等しい（または略等しい）圧力である１気圧（または略１気圧）に保持して熱処理を行うことが好ましい（請求項14、15）。

【００５０】以下、本発明を実施例により具体的に説明するが、本発明はこれらの例に限定されるものではない。

【００５１】

【実施例１】熱処理を行って光学特性が良好な蛍石を得るための本実施例にかかる製造装置は、熱処理対象の蛍石単結晶を収納した後に密閉されて真空排気される気密化可能な第１容器（ステンレス容器）と、該第１容器内に配置され蛍石単結晶及びフッ素化剤を収納する第２容器（カーボン容器）と、前記第１容器に接続された真空排気系と、前記第１容器の外側に配置されたヒーターとを有する。

【００５２】この装置を用いて、サイズφ200mm×50mmの蛍石を以下のスケジュール（全工程の所要日数：約13日、図１参照）に従って熱処理することにより、波長２５０ｎｍ以下の光リソグラフィーに使用可能な大口径（φ200mm以上）で光学特性が良好な蛍石単結晶を製造した。

［温度履歴］	［温度変化速度］	［所要時間］
20→1050℃	50 ℃/H	21H
1050→1050℃	－	24H
1050→900 ℃	2℃/H	75H
900→ 20 ℃	5 ℃/H	176H

即ち、本実施例の製造方法では、熱処理の最高温度を1050℃（1020～1150℃の範囲にある第１温度）として所定時間（24H）保持し、かつ前記第１温度より900℃（600～800℃の範囲或いは700～900℃の範囲にある第２温度）までの高温領域における冷却工程では、冷却速度を２℃/H（１℃/H以下）とした。

【００５３】また、前記第２温度より室温までの低温領域における冷却工程では、冷却速度を5 ℃/H（５℃/H以下）とした。製造した蛍石単結晶の複屈折と屈折率均質性を測定したところ、複屈折（光軸方向）の最大値が1.5nm/cm、側面歪（側面方向の複屈折）が5nm/cmであり、また屈折率均質性はΔn=1.2E-6、球面補正後のRMS(2乗平均平方根)が70E-4λ（λ=632.8nm）であり、波長２５０ｎｍ以下の光リソグラフィーに使用できる非常に良好な光学特性であった。

【００５４】本実施例では、冷却速度による処理物(蛍石単結晶)の光学特性向上に与える影響が特に大きい高温領域における冷却工程では、冷却を充分にゆっくりと行い、前記影響がそれよりも小さい低温領域における冷却工程では、速めに冷却することで、処理物(蛍石単結晶)の光学特性向上効果と生産性（納期及びコスト）と

のバランスをとっている。

【0055】そのため、本実施例によれば、屈折率の均質性がよく、複屈折が充分に小さくて、光リソグラフィーにおける光学系に使用可能な蛍石単結晶が得られ、特に波長２５０ｎｍ以下の光リソグラフィーに使用可能な大口径（φ200mm以上）で光学特性が良好な蛍石単結晶が得られるだけでなく、生産性（納期及びコスト）をも充分に満たすことができた。

【0056】

【実施例２】実施例１と同じ装置を用いて、サイズφ210mm×52mmの蛍石を以下のスケジュール（全工程の所要日数：約25日、図２参照）に従って熱処理することにより、波長２５０ｎｍ以下の光リソグラフィーに使用可能な大口径（φ200mm以上）で光学特性が良好な蛍石単結晶を製造した。

［温度履歴］	［温度変化速度］	［所要時間］
20→1080℃	30 ℃/H	35H
1080→1080℃	－	36H
1080→800 ℃	1℃/H	280H
800→ 20 ℃	3 ℃/H	260H

即ち、本実施例の製造方法では、熱処理の最高温度を1080℃（1020～1150℃の範囲にある第１温度）として所定時間（36H）保持し、かつ前記第１温度より800℃（600～800℃の範囲或いは700～900℃の範囲にある第２温度）までの高温領域における冷却工程では、冷却速度を１℃/H（２℃/H以下）とした。

【0057】また、前記第２温度より室温までの低温領域における冷却工程では、冷却速度を3 ℃/H（5℃/H以下）とした。製造した蛍石単結晶の複屈折と屈折率均質性を測定したところ、複屈折（光軸方向）の最大値が1.8nm/cm、側面歪（側面方向の複屈折）が4nm/cmであり、また屈折率均質性はΔn=1.8E−6、球面補正後のRMS(2乗平均平方根)が58E−4λ（λ=632.8nm）であり、波長２５０ｎｍ以下の光リソグラフィーに使用できる非常に良好な光学特性であった。

【0058】本実施例では、冷却速度による処理物(蛍石単結晶)の光学特性向上に与える影響が特に大きい高温領域における冷却工程では、冷却を充分にゆっくりと行い、前記影響がそれよりも小さい低温領域における冷却工程では、速めに冷却することで、処理物(蛍石単結晶)の光学特性向上効果と生産性（納期及びコスト）とのバランスをとっている。

【0059】そのため、本実施例によれば、屈折率の均質性がよく、複屈折が充分に小さくて、光リソグラフィーにおける光学系に使用可能な蛍石単結晶が得られ、特に波長２５０ｎｍ以下の光リソグラフィーに使用可能な大口径（φ200mm以上）で光学特性が良好な蛍石単結晶が得られるだけでなく、生産性（納期及びコスト）をも充分に満たすことができた。

【0060】

【比較例】実施例１と同一の装置を用いて、サイズφ200mm×50mmの蛍石を以下のスケジュール（全工程の所要日数：約12日、図３参照）に従って熱処理することにより蛍石単結晶を製造した。

［温度履歴］	［温度変化速度］	［所要時間］
20→1050℃	50 ℃/H	21H
1050→1050℃	－	24H
1050→900 ℃	3℃/H	50H
900→ 20 ℃	5 ℃/H	176H

即ち、本比較例の製造方法では、熱処理の最高温度を1050℃として所定時間（24H）保持した後、生産性を良くするために900℃までを3℃/Hの速度で冷却した。そして、900℃から室温までは冷却速度を5 ℃/Hとした。

【0061】製造した蛍石単結晶の複屈折と屈折率均質性を測定したところ、複屈折（光軸方向）の最大値が3.2nm/cm、側面歪（側面方向の複屈折）が16nm/cmであり、波長２５０ｎｍ以下の光リソグラフィーに使用できる光学特性ではなかった。即ち、本比較例では、冷却速度による処理物(蛍石単結晶)の光学特性向上に与える影響が特に大きい高温領域における冷却工程での冷却が速すぎたため、波長２５０ｎｍ以下の光リソグラフィーに使用できる良好な光学特性を有する蛍石単結晶を得ることができなかった。

【0062】

【発明の効果】以上説明したように、本発明によれば、屈折率の均質性がよく、複屈折が充分に小さくて、光リソグラフィーにおける光学系に使用可能な蛍石単結晶が得られ、特に波長２５０ｎｍ以下の光リソグラフィーに使用可能な大口径（φ200mm以上）で光学特性が良好な蛍石単結晶が得られる。

【0063】或いは、本発明によれば、大口径（φ200mm以上）で光学特性が良好な蛍石単結晶が得られるばかりか、生産性（納期及びコスト）をも充分に満たすことができる。本発明により、φ200mm以上の大きな蛍石においてはこれまで不可能であった複屈折の小さい蛍石を得ることが可能となり、光（波長250nm以下）リソグラフィー用の蛍石として実用に耐えるものが供給できるようになった。また、屈折率の均質性に関しても、充分な均質度に達するものであった。

【0064】また、熱処理に要する時間は２～４週間であり、生産上特に問題となる時間ではなく、コストアップも最小限に抑えることができた。

【0065】

【図面の詳細な説明】

【0066】

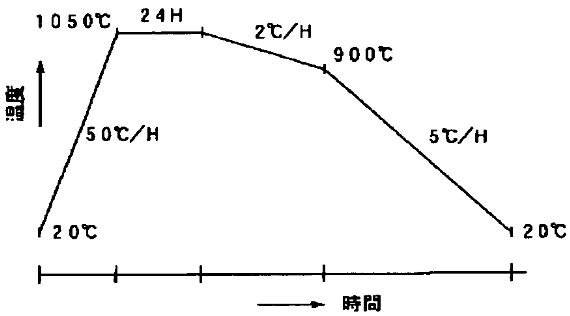
【図１】は、実施例１の熱処理スケジュールを示す履歴図である。

【0067】

【図２】は、実施例２の熱処理スケジュールを示す履歴図である。

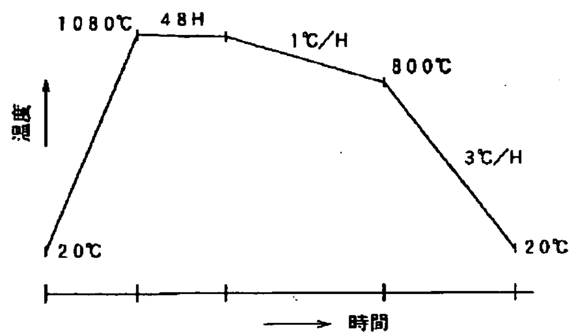
【0068】
【図3】は、従来（比較例）の熱処理スケジュールを示す履歴図である。
以上

【図1】



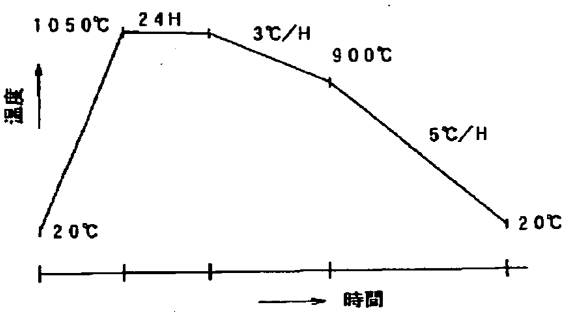
実施例1に記載の熱処理スケジュール

【図2】



実施例2に記載した熱処理スケジュール

【図3】



比較例に記載した熱処理スケジュール

フロントページの続き

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* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] After containing a fluorite single crystal, sealing said container and carrying out evacuation of the inside of said container into the container [-izing / a container], it heats at the heater formed in the outside of said container. airtight -- The process to which the temperature up of the temperature in a container is carried out to predetermined temperature (the 1st temperature) lower than the melting point of said fluorite single crystal, In the approach of manufacturing the fluorite single crystal which raised the optical property by looking the temperature in said container like [said predetermined temperature (the 1st temperature)] with predetermined time amount, the process to hold, and the process which lowers the temperature in said container to a room temperature, and heat-treating a fluorite single crystal more The manufacture approach of the fluorite single crystal characterized by making the maximum temperature of heat treatment into the predetermined temperature (the 1st temperature) in the range of 1020-1150 degrees C.
[Claim 2] After installing the 2nd container which contained the fluorite single crystal and the fluorination agent in the 1st container [-izing / the container], sealing said 1st container and carrying out evacuation of the inside of said 1st container, it heats at the heater formed in the outside of said 1st container. airtight -- While carrying out the temperature up of the temperature in the 1st container, and/or the temperature in the 2nd container to predetermined temperature (the 1st temperature) lower than the melting point of said fluorite single crystal The process which makes the inside of said 2nd container a fluorine gas ambient atmosphere, and the temperature in said 1st container and/or the temperature in the 2nd container Time amount predetermined to said predetermined temperature (the 1st temperature), and the process to hold, In the process which lowers the temperature in said 1st container, and/or the temperature in the 2nd container to a room temperature, the process which carries out atmospheric-air disconnection of the inside of said 1st container, and the method of manufacturing the fluorite single crystal which raised the optical property by it being alike and heat-treating a fluorite single crystal more The manufacture approach of the fluorite single crystal characterized by making the maximum temperature of heat treatment into the predetermined temperature (the 1st temperature) in the range of 1020-1150 degrees C.
[Claim 3] The manufacture approach according to claim 1 or 2 characterized by carrying out the cooling rate from said maximum temperature (the 1st temperature) to a room temperature in 2 degrees C/hour or less.
[Claim 4] The manufacture approach according to claim 1 or 2 characterized by carrying out the cooling rate to the predetermined temperature (the 2nd temperature) which is in the range of 600-800 degrees C, or the range of 700-900 degrees C (or those neighborhoods) from said maximum temperature (the 1st temperature) in 2 degrees C/hour or less.
[Claim 5] The manufacture approach according to claim 4 characterized by carrying out the cooling rate from said 2nd temperature to a room temperature in 5 degrees C/hour or less.
[Claim 6] The manufacture approach given in either of claims 1-5 characterized by obtaining the fluorite single crystal of the diameter of macrostomia usable to the optical system for optical lithography (more than phi200mm).
[Claim 7] The manufacture approach according to claim 6 that refractive-index difference **n is characterized by obtaining 2xten to six or less fluorite single crystal.
[Claim 8] The manufacture approach according to claim 6 or 7 that the value of the birefringence in the direction of an optical axis is characterized by obtaining the fluorite single crystal of 2 or less nm/cm.
[Claim 9] The manufacture approach according to claim 6 to 8 that the value of the birefringence in the direction of a side face perpendicular to the direction of an optical axis is characterized by obtaining a 5nm [/cm] or less fluorite single crystal.
[Claim 10] The fluorite single crystal for optical (wavelength of 250nm or less) lithography whose value of the birefringence in the direction of an optical axis is 2 or less nm/cm in the diameter of macrostomia (more than phi200mm).
[Claim 11] The fluorite single crystal according to claim 10 whose value of the birefringence in the direction of a side

face perpendicular to the direction of an optical axis is 5 or less nm/cm.
[Claim 12] The fluorite single crystal according to claim 10 or 11 whose refractive-index difference **n is 2x10 to six or less.
[Claim 13] After containing a fluorite single crystal, sealing said container and carrying out evacuation of the inside of said container into the container [-izing / a container], it heats at the heater formed in the outside of said container. airtight -- The process to which the temperature up of the temperature in a container is carried out to predetermined temperature lower than the melting point of said fluorite single crystal, In the approach of manufacturing the fluorite single crystal which raised the optical property by looking the temperature in said container like [said predetermined temperature] with predetermined time amount, the process to hold, and the process which lowers the temperature in said container to a room temperature, and heat-treating a fluorite single crystal more At the cooling process in a large elevated-temperature field, the effect which it has on the improvement in an optical property of the processing object (fluorite single crystal) by the cooling rate especially Cool slowly enough and said effect at the cooling process in a low-temperature field (it is a low-temperature field from an elevated-temperature field) smaller than it The manufacture approach of the fluorite single crystal characterized by balancing the improvement effectiveness in an optical property of a processing object (fluorite single crystal), and productivity (time for delivery and cost) by cooling speed.
[Claim 14] After containing a fluorite single crystal, sealing said container and carrying out evacuation of the inside of said container into the container [-izing / a container], it heats at the heater formed in the outside of said container. airtight -- The process to which the temperature up of the temperature in a container is carried out to predetermined temperature lower than the melting point of said fluorite single crystal, In the approach of manufacturing the fluorite single crystal which raised the optical property by looking the temperature in said container like [said predetermined temperature] with predetermined time amount, the process to hold, and the process which lowers the temperature in said container to a room temperature, and heat-treating a fluorite single crystal more The manufacture approach of the fluorite single crystal characterized by enclosing inert gas in said container, and heat-treating by holding the pressure in said container in one atmospheric pressure (or abbreviation 1 atmospheric pressure) in order to prevent oxidation of the fluorite single crystal at the time of heat treatment.
[Claim 15] After installing the 2nd container which contained the fluorite single crystal and the fluorination agent in the 1st container [-izing / the container], sealing said 1st container and carrying out evacuation of the inside of said 1st container, it heats at the heater formed in the outside of said 1st container. airtight -- While carrying out the temperature up of the temperature in the 1st container, and/or the temperature in the 2nd container to predetermined temperature lower than the melting point of said fluorite single crystal The process which makes the inside of said 2nd container a fluorine gas ambient atmosphere, and the temperature in said 1st container and/or the temperature in the 2nd container Time amount predetermined to said predetermined temperature, and the process to hold, In the process which lowers the temperature in said 1st container, and/or the temperature in the 2nd container to a room temperature, the process which carries out atmospheric-air disconnection of the inside of said 1st container, and the method of manufacturing the fluorite single crystal which raised the optical property by it being alike and heat-treating a fluorite single crystal more The manufacture approach of the fluorite single crystal which is made to evaporate said fluorination agent, and makes the inside of said 2nd container a fluorine gas ambient atmosphere, and is characterized by heat-treating by holding the pressure in said 1st container in one atmospheric pressure (or abbreviation 1 atmospheric pressure) in order to prevent oxidation of the fluorite single crystal at the time of heat treatment at least.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] The various devices by which KrF, an ArF excimer laser, and F2 laser were used for this invention To optical system, such as (for example, lenses, such as a stepper, a CVD system, and a fusion device) and aperture material It is especially optical lithography equipment (for example, it KrF(s)) with a wavelength of 250nm or less. The manufacture approach by which it uses for the optical system in the optical lithography equipment using an ArF excimer laser or F2 laser, and a fluorite single crystal with a good optical property is obtained with the suitable diameter of macrostomia (more than phi200mm), It is related with the fluorite single crystal for optical (wavelength of 250nm or less) lithography.
[0002]
[Description of the Prior Art] It sets at recent years, and it is integrated highly increasingly, VLSI has advanced features, and system-on-chip-ization in which a big system is incorporated by the chip top is advancing in the field of Logic VLSI. In connection with this, micro-processing-izing and high integration are demanded on wafers, such as silicon used as the substrate. And the aligner called a stepper in the optical lithography which exposes and imprints the detailed pattern of an integrated circuit on wafers, such as silicon, is used.
[0003] If DRAM is mentioned as an example in VLSI, the capacity beyond recent-years 256M will become actual, and processing line breadth is 0.35 micrometers. Since it is detailed the following, it licks in that of an optical lithography technique, and comes out, and the high image formation engine performance (resolution, depth of focus) is demanded of a certain stepper's projection lens. Resolution and the depth of focus are decided by the wavelength of light and NA (numerical aperture) of a lens which are used for exposure.
[0004] If NA of a lens is not large, it becomes impossible to incorporate the diffracted light, since the include angle of the diffracted light becomes [the exposure wavelength lambda] large in a finer pattern in being the same. Moreover, since the include angle of the diffracted light in the same pattern becomes small so that the exposure wavelength lambda is short, NA of a lens may be small. Resolution and the depth of focus are expressed by the degree type.
[0005] Resolution =k1 and the lambda/NA depth of focus = lambda [k2 and]/2 (here, k1 and k2 are a proportionality constant)
in order to raise resolution from an upper type -- NA of a lens -- large -- carrying out (a lens being diameter[of macrostomia]-ized) -- or it turns out that it is more advantageous to shorten lambda in respect of the depth of focus that what is necessary is just to shorten exposure wavelength lambda.
[0006] First, if short wavelength-ization of light is described, the exposure wavelength lambda will turn into short wavelength gradually, and the stepper who makes the light source KrF excimer laser light (wavelength of 248nm) will also have come to appear in a commercial scene. 250 In the short wavelength field below nm, there are very few optical materials which can be used as an object for optical lithography, and fluorite and two kinds of ingredients of quartz glass are used.
[0007] Next, if diameter-ization of macrostomia of a lens is described, quartz glass and a fluorite single crystal excellent in the optical properties of the refractive index instead of the thing that what is necessary is just only a diameter of macrostomia, such as homogeneity, will be required. Here, the manufacture approach (an example) of the conventional fluorite single crystal is shown. The fluorite single crystal is manufactured by the Bridgman method (the stock hamburger method, crucible method of descent).
[0008] In the case of the fluorite single crystal used in an ultraviolet region or a vacuum-ultraviolet region, it is common to use the high grade raw material produced by chemosynthesis without natural fluorite as a raw material. Although a raw material can be used with powder, since the volume decrease when fusing in this case is intense, usually a half-

melting article and its grinding article are used.
[0009] First, the crucible filled up with said raw material is placed into training equipment, and the inside of training equipment is held in the vacuum ambient atmosphere of 10-3 to ten to 4 Pa. Next, the temperature in training equipment is raised to more than the melting point of fluorite, and the raw material in a crucible is fused. Under the present circumstances, in order to suppress time fluctuation of the temperature in training equipment, the control or the highly precise PID control by the constant power output is performed.
[0010] It is made to crystallize gradually from the lower part of a crucible in a crystal training phase by reducing a crucible at the rate of 0.1 - 5 mm/h extent. Quenching is avoided in the place crystallized to the melt topmost part so that the crystal (ingot) which ended crystal training and was raised may not break, and easy annealing is performed. In the place where the temperature in training equipment fell to room temperature extent, atmospheric-air disconnection of the equipment is carried out, and an ingot is taken out.
[0011] In the case of the fluorite used for the aperture material as which neither an optic with small size nor homogeneity is required, after cutting an ingot, even a final product is processed through the process of slight roundness etc. On the other hand, it is used for a stepper's projection lens etc., and when it is the fluorite single crystal with which high homogeneity is demanded, easy annealing is performed with an ingot. And after cutting processing is carried out, annealing is further performed in magnitude suitable according to the target product.
[0012] By the way, when the fluorite for optical lithography is indicated by JP,8-5801,A and it is used for it in a specific wavelength band 350nm or less, also in which direction of the direction of 3 coordinates, the fluorite whose optical path difference by the birefringence is 10 or less nm/cm is indicated. The optical path difference is expressed with the numeric value what time of wavelength the effect which it has on the image formation engine performance of optical system is, and effect has that the multiplier is small (for example, so little lambda/10 etc.). For example, in the case of 10nm of optical path difference, on the wavelength of lambda= 248nm, the optical path difference is 10/248=0.040lambda, and the optical path difference becomes with 10/193=0.052lambda by lambda= 193nm.
[0013] That is, even if it is 10nm of the same optical path difference, as effectiveness, lambda= 193nm of effect is larger and the image formation engine performance gets worse. Therefore, in a stepper's projection lens using a next-generation ArF excimer laser (wavelength of 193nm), fluorite with still inadequate optical-path-difference 10 nm/cm and the still smaller optical path difference by the birefringence is needed.
[0014] In addition, in the following, the thing of the optical path difference per unit length by the birefringence is only called a birefringence. Moreover, generally this birefringence is called distortion in many cases. This is for therefore producing a birefringence distorted in many cases, even when there is no birefringence in the ingredient itself.
[0015]
[Problem(s) to be Solved by the Invention] As mentioned above, fluorite is manufactured by the Bridgman method. And after growing up fluorite with the usual Bridgman method, to extent into which fluorite is not broken, it cools slowly (to or extent which can be cut), and takes out as an ingot. Although it may start directly in the size made into the purpose from an ingot, since a birefringence and refractive-index heterogeneity become larger as the volume increases, quality is raised by applying to a heat treatment process further after cutting to two or more blocks.
[0016] The period of this heat treatment process was setting the cooling rate in a cooling process (process) with about two common therefore weeks and the large time amount pulse duty factor to the whole heat treatment process to 10 degrees C/H-5-degree-C/H from one week by the former in view of productivity. However, the fluorite single crystal obtained by annealing (heat treatment) of such a fluorite single crystal had the trouble that the homogeneity of a refractive index was bad and a birefringence was too large.
[0017] Therefore, there was a trouble that the fluorite single crystal which can be used for the optical system in optical lithography was hard to be obtained, and the fluorite single crystal of the diameter of macrostomia (more than phi200mm) which can be used especially for optical lithography with a wavelength of 250nm or less was not obtained. It aims at offering the manufacture approach of the fluorite single crystal with which a fluorite single crystal usable to optical system [in / the homogeneity of a refractive index is good by making this invention in view of this trouble, and heat-treating a fluorite single crystal, and a birefringence is fully small, and / optical lithography] is obtained, and a fluorite single crystal with a good optical property is obtained with the diameter of macrostomia usable to especially optical lithography with a wavelength of 250nm or less (more than phi200mm).
[0018] Or this invention aims at an optical property not only doing so the effectiveness that a good fluorite single crystal is obtained, with said diameter of macrostomia (more than phi200mm), but offering the manufacture approach of a fluorite single crystal that this effectiveness and productivity were able to be balanced. Or this invention aims at offering the fluorite single crystal for optical (wavelength of 250nm or less) lithography.
[0019]

[Means for Solving the Problem] After containing a fluorite single crystal, sealing said container and carrying out evacuation of the inside of said container into the container [-izing / a container], it heats at the heater formed in the outside of said container. therefore, this invention -- the first -- "-- airtight -- The process to which the temperature up of the temperature in a container is carried out to predetermined temperature (the 1st temperature) lower than the melting point of said fluorite single crystal, In the approach of manufacturing the fluorite single crystal which raised the optical property by looking the temperature in said container like [said predetermined temperature (the 1st temperature)] with predetermined time amount, the process to hold, and the process which lowers the temperature in said container to a room temperature, and heat-treating a fluorite single crystal more The manufacture approach (claim 1) of the fluorite single crystal characterized by making the maximum temperature of heat treatment into the predetermined temperature (the 1st temperature) in the range of 1020-1150 degrees C" is offered.
[0020] Install the 2nd container which contained the fluorite single crystal and the fluorination agent in the 1st container [-izing / the container], and said 1st container is sealed. moreover, this invention -- the second -- "-- airtight -- After carrying out evacuation of the inside of said 1st container, it heats at the heater formed in the outside of said 1st container. While carrying out the temperature up of the temperature in the 1st container, and/or the temperature in the 2nd container to predetermined temperature (the 1st temperature) lower than the melting point of said fluorite single crystal The process which makes the inside of said 2nd container a fluorine gas ambient atmosphere, and the temperature in said 1st container and/or the temperature in the 2nd container Time amount predetermined to said predetermined temperature (the 1st temperature), and the process to hold, In the process which lowers the temperature in said 1st container, and/or the temperature in the 2nd container to a room temperature, the process which carries out atmospheric-air disconnection of the inside of said 1st container, and the method of manufacturing the fluorite single crystal which raised the optical property by it being alike and heat-treating a fluorite single crystal more The manufacture approach (claim 2) of the fluorite single crystal characterized by making the maximum temperature of heat treatment into the predetermined temperature (the 1st temperature) in the range of 1020-1150 degrees C" is offered.
[0021] Moreover, this invention provides the third with "the manufacture approach (claim 3) according to claim 1 or 2 characterized by carrying out the cooling rate from said maximum temperature (the 1st temperature) to a room temperature in 2 degrees C/hour or less." Moreover, this invention provides the fourth with "the manufacture approach (claim 4) according to claim 1 or 2 characterized by carrying out the cooling rate to the predetermined temperature (the 2nd temperature) which is in the range of 600-800 degrees C, or the range of 700-900 degrees C (or those neighborhoods) from said maximum temperature (the 1st temperature) in 2 degrees C/hour or less."
[0022] Moreover, this invention provides the fifth with "the manufacture approach (claim 5) according to claim 4 characterized by carrying out the cooling rate from said 2nd temperature to a room temperature in 5 degrees C/hour or less." Moreover, this invention provides the sixth with "the manufacture approach (claim 6) given in either of claims 1-5 characterized by obtaining the fluorite single crystal of the diameter of macrostomia usable to the optical system for optical lithography (more than phi200mm)."
[0023] Moreover, this invention provides the seventh with "the manufacture approach (claim 7) according to claim 6 that refractive-index difference **n is characterized by obtaining 2xten to six or less fluorite single crystal." Moreover, this invention provides the eighth with "the manufacture approach (claim 8) according to claim 6 or 7 that the value of the birefringence in the direction of an optical axis is characterized by obtaining the fluorite single crystal of 2 or less nm/cm."
[0024] Moreover, this invention provides the ninth with "the manufacture approach (claim 9) according to claim 6 to 8 that the value of the birefringence in the direction of a side face perpendicular to the direction of an optical axis is characterized by obtaining the fluorite single crystal of 5 or less nm/cm." Moreover, this invention provides the tenth with "the fluorite single crystal (claim 10) for optical (wavelength of 250nm or less) lithography whose value of the birefringence in the direction of an optical axis is 2 or less nm/cm in the diameter of macrostomia (more than phi200mm)."
[0025] Moreover, this invention provides the eleventh with "the fluorite single crystal (claim 11) according to claim 10 whose value of the birefringence in the direction of a side face perpendicular to the direction of an optical axis is 5 or less nm/cm." Moreover, this invention provides the twelfth with "the fluorite single crystal (claim 12) according to claim 10 or 11 whose refractive-index difference **n is 2x10 to six or less." After containing a fluorite single crystal, sealing said container and carrying out evacuation of the inside of said container into the container [-izing / a container], it heats at the heater formed in the outside of said container. moreover, this invention -- the thirteenth -- "-- airtight -- The process to which the temperature up of the temperature in a container is carried out to predetermined temperature lower than the melting point of said fluorite single crystal, In the approach of manufacturing the fluorite single crystal which raised the optical property by looking the temperature in said container like [said predetermined

temperature] with predetermined time amount, the process to hold, and the process which lowers the temperature in said container to a room temperature, and heat-treating a fluorite single crystal more At the cooling process in a large elevated-temperature field, the effect which it has on the improvement in an optical property of the processing object (fluorite single crystal) by the cooling rate especially Cool slowly enough and said effect at the cooling process in a low-temperature field (it is a low-temperature field from an elevated-temperature field) smaller than it The manufacture approach (claim 13) of the fluorite single crystal characterized by balancing the improvement effectiveness in an optical property of a processing object (fluorite single crystal) and productivity (time for delivery and cost) by cooling speed" is offered.

[0026] After containing a fluorite single crystal, sealing said container and carrying out evacuation of the inside of said container into the container [-izing / a container], it heats at the heater formed in the outside of said container. moreover, this invention -- the 14th -- "-- airtight -- The process to which the temperature up of the temperature in a container is carried out to predetermined temperature lower than the melting point of said fluorite single crystal, In the approach of manufacturing the fluorite single crystal which raised the optical property by looking the temperature in said container like [said predetermined temperature] with predetermined time amount, the process to hold, and the process which lowers the temperature in said container to a room temperature, and heat-treating a fluorite single crystal more In order to prevent oxidation of the fluorite single crystal at the time of heat treatment, the manufacture approach (claim 14) of the fluorite single crystal characterized by enclosing inert gas in said container, and heat-treating by holding the pressure in said container in one atmospheric pressure (or abbreviation 1 atmospheric pressure)" is offered.

[0027] Install the 2nd container which contained the fluorite single crystal and the fluorination agent in the 1st container [-izing / the container], and said 1st container is sealed. moreover, this invention -- the 15th -- "-- airtight -- After carrying out evacuation of the inside of said 1st container, while heating at the heater formed in the outside of said 1st container and carrying out the temperature up of the temperature in the 1st container, and/or the temperature in the 2nd container to predetermined temperature lower than the melting point of said fluorite single crystal The process which makes the inside of said 2nd container a fluorine gas ambient atmosphere, and the temperature in said 1st container and/or the temperature in the 2nd container Time amount predetermined to said predetermined temperature, and the process to hold, In the process which lowers the temperature in said 1st container, and/or the temperature in the 2nd container to a room temperature, the process which carries out atmospheric-air disconnection of the inside of said 1st container, and the method of manufacturing the fluorite single crystal which raised the optical property by it being alike and heat-treating a fluorite single crystal more In order to prevent oxidation of the fluorite single crystal at the time of heat treatment at least, make said fluorination agent evaporate and the inside of said 2nd container is made into a fluorine gas ambient atmosphere. And the manufacture approach (claim 15) of the fluorite single crystal characterized by heat-treating by holding the pressure in said 1st container in one atmospheric pressure (or abbreviation 1 atmospheric pressure)" is offered.

[0028]

[Embodiment of the Invention] In what kind of equipment and ambient atmosphere heat treatment (annealing) which raises the optical property of a fluorite single crystal (for example, a birefringence is made small) and which is performed for accumulating is not only performed, but it becomes the important point to what kind of schedule it is carried out. For example, the maximum temperature of heat treatment is what degree C, and the schedule of in how many hours a temperature up is carried out from a room temperature to a maximum temperature and when it is made to cool to a room temperature in between after holding in between when by the maximum temperature becomes important.

[0029] Then, when this invention persons inquired wholeheartedly, as a maximum temperature, it found out that 1020-1150 degrees C was the optimal. That is, above 1150 degrees C, it turned out that there is little annealing effectiveness which the defect leading to dispersion becomes easy to generate inside fluorite, and is given to improvement in an optical property below 1020 degrees C. So, the maximum temperature of heat treatment was made into the predetermined temperature (the 1st temperature) in the range of 1020-1150 degrees C by the manufacture approach concerning this invention (claims 1-9).

[0030] And according to this invention (claims 1-9), a fluorite single crystal the homogeneity of a refractive index is good, small [fully] a birefringence and usable to the optical system in optical lithography is obtained, and a fluorite single crystal with a good optical property is obtained by especially optical lithography with a wavelength of 250nm or less with the usable diameter of macrostomia (more than phi200mm). In addition, although the holding time of said maximum temperature should just be about 24 hours, lengthening is desirable [the holding time] if the aperture and the volume of a processing object (fluorite single crystal) become large.

[0031] Moreover, the programming rate from a room temperature to a maximum temperature is good to set up in the range which the bad influence to the processing object (fluorite single crystal) by the thermal shock does not generate.

Next, although it is the cooling process after carrying out predetermined time maintenance at said maximum temperature, this process is important for especially improvement in an optical property of a processing object (fluorite single crystal). That is, sufficient effectiveness will not be acquired, if the improvement effectiveness of an optical property becomes large and a cooling rate is too quicker conversely, as a cooling rate is made late.

[0032] So, by the manufacture approach concerning this invention (claim 3), the cooling rate from said maximum temperature (the 1st temperature) to a room temperature was carried out in 2 degrees C/hour or less. Moreover, this invention persons found out that especially the effect that the cooling rate in the cooling process of an elevated-temperature field of resulting in the predetermined temperature (the 2nd temperature) which is in the range of 600-800 degrees C (or the neighborhood) or the range of 700-900 degrees C (or the neighborhood) from a maximum temperature has on the improvement in an optical property of a processing object (fluorite single crystal) was large.

[0033] So, by the manufacture approach concerning this invention (claim 4), the cooling rate to the predetermined temperature (the 2nd temperature) which is in the range of 600-800 degrees C or the range of 700-900 degrees C (or those neighborhoods) from said maximum temperature (the 1st temperature) was carried out in 2 degrees C/hour or less. According to this invention (claims 3 and 4), a fluorite single crystal with a very good optical property is obtained by optical lithography with a wavelength of 250nm or less with the usable diameter of macrostomia (more than phi200mm).

[0034] By the way, since the die length of a cooldown delay influences productivity (time for delivery and cost) greatly, from the point, its way that a cooldown delay is short as much as possible (a cooling rate is quick) is good. Then, although this invention persons cool slowly enough at the cooling process in the elevated-temperature field where the effect which it has on the improvement in an optical property of the processing object (fluorite single crystal) by the cooling rate is especially large as mentioned above At the cooling process in a low-temperature field (it is a low-temperature field from an elevated-temperature field) smaller than it, said effect decided to balance the improvement effectiveness in an optical property of a processing object (fluorite single crystal), and productivity (time for delivery and cost) by cooling speed (claim 13).

[0035] By the manufacture approach concerning this invention (claim 5), the cooling rate in the elevated-temperature field to the predetermined temperature (the 2nd temperature) which is in the range of 600-800 degrees C or the range of 700-900 degrees C (or those neighborhoods) from said maximum temperature (the 1st temperature) was carried out in 2 degrees C/hour or less, and, specifically, the cooling rate in the low-temperature field from said 2nd temperature to a room temperature was further carried out in 5 degrees C/hour or less.

[0036] Therefore, an optical property not only does so said effectiveness that a good fluorite single crystal is obtained, with the diameter of macrostomia (more than phi200mm), but according to this invention (claim 5), it can balance this effectiveness and productivity. Thus, in heat treatment concerning the fluorite of the diameter of macrostomia (more than phi200mm), what (cooling rate : 2 degrees C/(hour) or less) the effect which it has on the improvement in an optical property of the processing object (fluorite single crystal) by the cooling rate cools very slowly at the large cooling process of an elevated-temperature field especially is important.

[0037] For example, by having cooled the (elevated-temperature field) at the too quick rate of 3 degrees C/hour from a maximum temperature to 900 degrees C, fluorite with a good optical property is not obtained like the example of a comparison mentioned later. Moreover, it is better for cooling not much rapidly also at the cooling process in a subsequent low-temperature field to avoid.

[0038] In addition, it is desirable to make the cooling process (cooling process especially in an elevated-temperature field) in an elevated-temperature field and/or a low-temperature field into two or more steps (for a cooling rate to be two or more kinds) from a single stage story (for a cooling rate to be one kind) with enlargement of a processing object (fluorite single crystal). that is, what (the cooling process of a rate later than the cooling rate in a single stage story -- 1 -- or it adds two or more) the cooling process (cooling process especially in an elevated-temperature field) in an elevated-temperature field and/or a low-temperature field is subdivided for within limits which a processing object (fluorite single crystal) enlarges, and which are alike and take and fully fulfill productivity (time for delivery and cost) is desirable.

[0039] In addition, the temperature requirement of the whole elevated-temperature field and/or the whole low-temperature field may be extended with increase of the number of fragmentation in this case. Moreover, it is desirable to set the temperature requirement where the 2nd temperature is included as the higher range with enlargement of a processing object (fluorite single crystal) within limits which fully fulfill productivity (time for delivery and cost) (for it to shift to an elevated-temperature side), or to reduce a temperature requirement.

[0040] For example, the range of 600-800 degrees C or the range of 700-900 degrees C (or those neighborhoods), and the temperature requirement where the 2nd set-up temperature is included are followed on enlargement of a processing

object (fluorite single crystal). Within limits which fully fulfill productivity (time for delivery and cost), it is desirable to change into the high range or the narrow range like 650-850 degrees C, 750-950 degrees C, 700-800 degrees C, 800-900 degrees C, 800-850 degrees C, 850-900 degrees C, and 900-950 degrees C.

[0041] Or it is desirable to combine suitably the shift by the side of the elevated temperature of the escape of the temperature requirement where fragmentation of a cooling process and the 2nd temperature are included or contraction, and each temperature field with enlargement of a processing object (fluorite single crystal) within limits which fully fulfill productivity (time for delivery and cost). Even if a processing object (fluorite single crystal) is further enlarged by making it this configuration, an optical property can also fully fill about [that a good fluorite single crystal can be obtained] and productivity (time for delivery and cost) with the usable diameter of macrostomia to optical lithography with a wavelength of 250nm or less.

[0042] The manufacture approach of the fluorite single crystal concerning this invention (claim 13) is effective when obtaining the fluorite single crystal of the usable diameter of macrostomia (more than phi200mm) to the optical system for optical lithography with a wavelength of 250nm or less. The manufacture approach of the fluorite single crystal concerning this invention (claim 13) is effective when usable refractive-index difference **n obtains the fluorite single crystal of the diameter of macrostomia (more than phi200mm) or less by 2x10 to six to the optical system for optical lithography with a wavelength of 250nm or less.

[0043] The manufacture approach of the fluorite single crystal concerning this invention (claim 13) is effective when the value of the birefringence in the direction of an optical axis usable to the optical system for optical lithography with a wavelength of 250nm or less obtains the fluorite single crystal of the diameter of macrostomia (more than phi200mm) by 2 or less nm/cm. Moreover, the manufacture approach of the fluorite single crystal concerning this invention (claim 13) is effective when the value of the birefringence in the direction of a side face perpendicular to the direction of an optical axis usable to the optical system for optical lithography with a wavelength of 250nm or less obtains the fluorite single crystal of the diameter of macrostomia (more than phi200mm) by 5 or less nm/cm.

[0044] The manufacture approach of the fluorite single crystal concerning this invention (claims 1-5) is effective when obtaining the fluorite single crystal of the usable diameter of macrostomia (more than phi200mm) to the optical system for optical lithography with a wavelength of 250nm or less (claim 6). Moreover, the manufacture approach of the fluorite single crystal concerning this invention (claims 1-5) is effective when usable refractive-index difference **n obtains the fluorite single crystal of the diameter of macrostomia (more than phi200mm) or less by 2x10 to six to the optical system for optical lithography with a wavelength of 250nm or less (claim 7).

[0045] Moreover, the manufacture approach of the fluorite single crystal concerning this invention (claims 1-5) is effective when the value of the birefringence in the direction of an optical axis usable to the optical system for optical lithography with a wavelength of 250nm or less obtains the fluorite single crystal of the diameter of macrostomia (more than phi200mm) by 2 or less nm/cm (claim 8). Moreover, the manufacture approach of the fluorite single crystal concerning this invention (claims 1-5) is effective when the value of the birefringence in the direction of a side face perpendicular to the direction of an optical axis usable to the optical system for optical lithography with a wavelength of 250nm or less obtains the fluorite single crystal of the diameter of macrostomia (more than phi200mm) by 5 or less nm/cm (claim 9).

[0046] Thus, this invention enables it to obtain the small fluorite of the birefringence which was impossible until now in the big fluorite beyond phi200mm, and what is equal to practical use as fluorite (for example, it is used for a projection lens) for optical (wavelength of 250nm or less) lithography can be supplied now. Moreover, it was what becomes whenever [sufficient homogeneity] also about the homogeneity of a refractive index.

[0047] That is, although the fluorite single crystal for the optical (wavelength of 250nm or less) lithography of the diameter of macrostomia (more than phi200mm) with the small and value of the birefringence indicated by claims 10-12 was not obtained until now, manufacture of it was attained by this invention (9 claim 1- 13). in addition -- although there are 360 rotations in the direction of a side face when measurement of a birefringence is followed in a direction (this is called the direction of an optical axis) perpendicular to a flat surface, and the direction (this is called the direction of a side face) perpendicular to it about a material (fluorite) with a diameter [of 200mm], and a thickness of 50mm -- measurement -- then, it turned out that it becomes the almost same value.

[0048] Moreover, in the direction of an optical axis, and the direction of a side face, the direction of the direction of a side face was found by that it is large more than twice as the optical path difference per unit length. As for the manufacturing installation concerning this invention to heat-treat and for an optical property obtain good fluorite, what has a container surrounding a processing object (fluorite) and has a heating means on the outside is good. Moreover, it is desirable during heat treatment for there to be no temperature unevenness in a processing object (fluorite).

[0049] Although it carries out in air about the ambient atmosphere of heat treatment in the ambient atmosphere, vacuum

ambient atmosphere, or fluorine gas ambient atmosphere of inert gas in order that oxidation reaction of fluorite may progress above 700 degrees C The deformation and destruction of a heat treatment container (airtight -- the container [-izing / a container], or the 1st container) by the differential pressure of the atmospheric pressure (outside of a container) and container internal pressure under an elevated-temperature condition are prevented. Consequently, so that the fluorite single crystal for optical (wavelength of 250nm or less) lithography may be stabilized and it may be obtained it is desirable to heat-treat by holding the pressure in said container or the 1st container in one atmospheric pressure (or abbreviation 1 atmospheric pressure) which is a pressure equal (or abbreviation -- equal) to atmospheric pressure (claims 14 and 15).
[0050] Hereafter, although an example explains this invention concretely, this invention is not limited to these examples.
[0051]
[Example 1] The manufacturing installation concerning this example to heat-treat and for an optical property obtain good fluorite evacuation is sealed and carried out after containing the fluorite single crystal for heat treatment -- airtight -- with the 1st container [-izing / the container] (stainless steel container) It has the 2nd container (carbon container) which is arranged in this 1st container and contains a fluorite single crystal and a fluorination agent, the evacuation system connected to said 1st container, and the heater arranged on the outside of said 1st container.
[0052] The optical property manufactured the good fluorite single crystal with the usable diameter of macrostomia (more than phi200mm) to optical lithography with a wavelength of 250nm or less using this equipment by heat-treating size phi200mmx50mm fluorite according to the following schedules (the necessary days of all processes: referring to drawing 1 for about 13 days).
[Temperature hysteresis] [Temperature-change rate] [Duration]
20->1050 degrees C 50 **/H 21H 1050 ->1050 degree C - 24H1050->900 ** 2-degree-C/H 75H 900 -> 20 ** 5 **/H
Predetermined time (24H) maintenance of the maximum temperature of heat treatment is carried out by 176H, i.e., the manufacture approach of this example, as 1050 degrees C (the 1st temperature in the range of 1020-1150 degrees C). And at the cooling process in the elevated-temperature field to 900 degrees C (the 2nd temperature in the range of 600-800 degrees C, or the range of 700-900 degrees C), the cooling rate was set to 2-degree-C/H (1 degree C/below H) from said 1st temperature.
[0053] Moreover, at the cooling process in the low-temperature field to a room temperature, the cooling rate was set to 5 **/H (5 degrees C/below H) from said 2nd temperature. When the birefringence of a fluorite single crystal and refractive-index homogeneity which were manufactured were measured, the maximum of a birefringence (the direction of an optical axis) was 1.5 nm/cm, side-face distortion (birefringence of the direction of a side face) was 5 nm/cm, and RMS after deltan=1.2E-6 and spherical-surface amendment (square mean square root) was 70E-4lambda (lambda= 632.8nm), and refractive-index homogeneity was a very good optical property which can be used for optical lithography with a wavelength of 250nm or less.
[0054] At this example, the effect which it has on the improvement in an optical property of the processing object (fluorite single crystal) by the cooling rate has balanced the improvement effectiveness in an optical property of a processing object (fluorite single crystal), and productivity (time for delivery and cost) at the cooling process in a large elevated-temperature field especially by cooling slowly enough and cooling speed at the cooling process in the low-temperature field where said effect is smaller than it.
[0055] Therefore, a fluorite single crystal with a good optical property is not only obtained by especially optical lithography with a wavelength of 250nm or less, but according to this example, the fluorite single crystal the homogeneity of a refractive index is good, small [fully] a birefringence and usable to the optical system in optical lithography was obtained, and it was fully able to fill productivity (time for delivery and cost) with the usable diameter of macrostomia (more than phi200mm) to it.
[0056]
[Example 2] The optical property manufactured the good fluorite single crystal with the usable diameter of macrostomia (more than phi200mm) to optical lithography with a wavelength of 250nm or less using the same equipment as an example 1 by heat-treating size phi210mmx52mm fluorite according to the following schedules (the necessary days of all processes: referring to drawing 2 for about 25 days).
[Temperature hysteresis] [Temperature-change rate] [Duration]
20->1080 degrees C 30 **/H 35H 1080 ->1080 degree C - 36H1080->800 ** 1-degree-C/H 280H 800 -> 20 ** 3 **/H
Predetermined time (36H) maintenance of the maximum temperature of heat treatment is carried out by 260H, i.e., the manufacture approach of this example, as 1080 degrees C (the 1st temperature in the range of 1020-1150 degrees C). And at the cooling process in the elevated-temperature field to 800 degrees C (the 2nd temperature in the range of 600-

800 degrees C, or the range of 700-900 degrees C), the cooling rate was set to 1-degree-C/H (2 degrees C/below H) from said 1st temperature.
[0057] Moreover, at the cooling process in the low-temperature field to a room temperature, the cooling rate was set to 3 **/H (5 degrees C/below H) from said 2nd temperature. When the birefringence of a fluorite single crystal and refractive-index homogeneity which were manufactured were measured, the maximum of a birefringence (the direction of an optical axis) was 1.8 nm/cm, side-face distortion (birefringence of the direction of a side face) was 4 nm/cm, and RMS after deltan=1.8E-6 and spherical-surface amendment (square mean square root) was 58E-4lambda (lambda= 632.8nm), and refractive-index homogeneity was a very good optical property which can be used for optical lithography with a wavelength of 250nm or less.
[0058] At this example, the effect which it has on the improvement in an optical property of the processing object (fluorite single crystal) by the cooling rate has balanced the improvement effectiveness in an optical property of a processing object (fluorite single crystal), and productivity (time for delivery and cost) at the cooling process in a large elevated-temperature field especially by cooling slowly enough and cooling speed at the cooling process in the low-temperature field where said effect is smaller than it.
[0059] Therefore, a fluorite single crystal with a good optical property is not only obtained by especially optical lithography with a wavelength of 250nm or less, but according to this example, the fluorite single crystal the homogeneity of a refractive index is good, small [fully] a birefringence and usable to the optical system in optical lithography was obtained, and it was fully able to fill productivity (time for delivery and cost) with the usable diameter of macrostomia (more than phi200mm) to it.
[0060]
[Comparative Example(s)] The fluorite single crystal was manufactured using the same equipment as an example 1 by heat-treating size phi200mmx50mm fluorite according to the following schedules (the necessary days of all processes: referring to drawing 3 for about 12 days).
[Temperature hysteresis] [Temperature-change rate] [Duration]
20->1050 degrees C 50 **/H 21H 1050 ->1050 degree C - 24H1050->900 ** 3-degree-C/H 50H 900 -> 20 ** 5 **/H By 176H, i.e., the manufacture approach of this example of a comparison, the maximum temperature of heat treatment was made into 1050 degrees C, and after carrying out predetermined time (24H) maintenance, in order to improve productivity, even 900 degrees C was cooled at the rate of 3 degrees C/H. And 900 degrees C to the room temperature set the cooling rate to 5 **/H.
[0061] When the birefringence of a fluorite single crystal and refractive-index homogeneity which were manufactured were measured, the maximum of a birefringence (the direction of an optical axis) was 3.2 nm/cm, side-face distortion (birefringence of the direction of a side face) was 16 nm/cm, and it was not the optical property which can be used for optical lithography with a wavelength of 250nm or less. That is, in this example of a comparison, since cooling at the cooling process in the elevated-temperature field where the effect which it has on the improvement in an optical property of the processing object (fluorite single crystal) by the cooling rate is especially large was too quick, the fluorite single crystal which has the good optical property which can be used for optical lithography with a wavelength of 250nm or less was not able to be obtained.
[0062]
[Effect of the Invention] As explained above, according to this invention, a fluorite single crystal the homogeneity of a refractive index is good, small [fully] a birefringence and usable to the optical system in optical lithography is obtained, and a fluorite single crystal with a good optical property is obtained by especially optical lithography with a wavelength of 250nm or less with the usable diameter of macrostomia (more than phi200mm).
[0063] Or according to this invention, about [that a fluorite single crystal with a good optical property is obtained] and productivity (time for delivery and cost) can also fully be filled with the diameter of macrostomia (more than phi200mm). This invention enables it to obtain the small fluorite of the birefringence which was impossible until now in the big fluorite beyond phi200mm, and what is equal to practical use as fluorite for optical (wavelength of 250nm or less) lithography can be supplied now. Moreover, it was what becomes whenever [sufficient homogeneity] also about the homogeneity of a refractive index.
[0064] Moreover, the time amount which heat treatment takes is two - four weeks, and not the time amount that poses a problem especially on production but the cost rise was able to suppress it to the minimum.
[0065]
[Detailed Description of the Drawings]
[0066]
[Drawing 1] It is the hysteresis Fig. showing ** and the heat treatment schedule of an example 1.

[0067]
[Drawing 2] It is the hysteresis Fig. showing ** and the heat treatment schedule of an example 2.
[0068]
[Drawing 3] It is the hysteresis Fig. showing ** and the heat treatment schedule of the former (example of a comparison).
Above

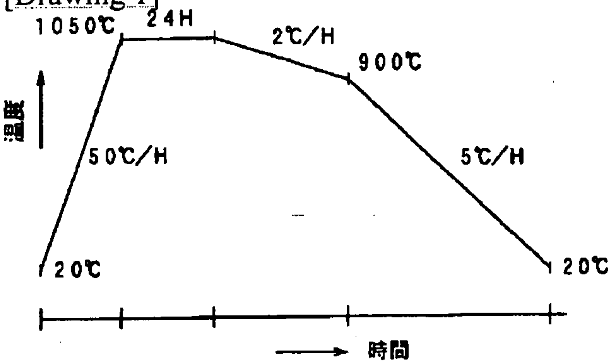
[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

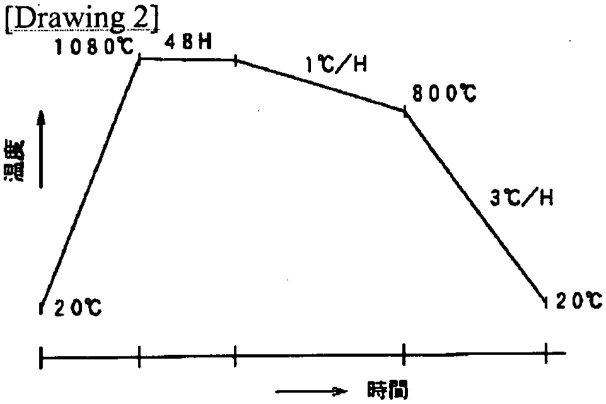
DRAWINGS

[Drawing 1]



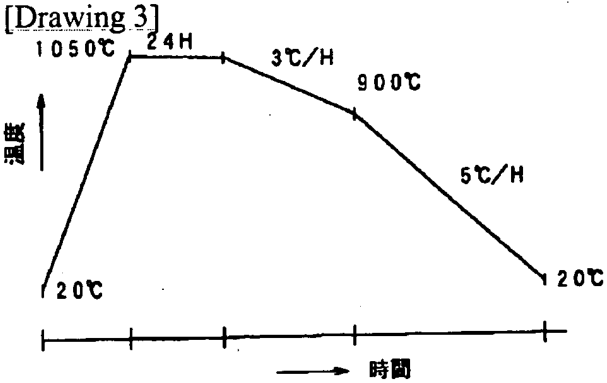
実施例1に記載の熱処理スケジュール

[Drawing 2]



実施例2に記載した熱処理スケジュール

[Drawing 3]



比較例に記載した熱処理スケジュール

[Translation done.]